

AD-A247 111



REPORT DOCUMENTATION PAGE

2

2a. SECURITY CLASSIFICATION AUTHORITY DTIC ELECTE			1b. RESTRICTIVE MARKINGS		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE MAR 10 1992			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 2			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Rensselaer Polytechnic Inst.		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research (Code 418)		
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry, RPI Troy, NY 12180-3590			7b. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington VA 22217		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-91-J-1917		
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street, Code 1513:ETF Arlington, VA 22217-5000			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO	PROJECT NO	TASK R8T NO 4134058-2
			WORK UNIT ACCESSION NO		
11. TITLE (Include Security Classification) Studies of 1,3-Disilacyclobutanes as Single-source CVD Precursors to Silicon Carbide					
12. PERSONAL AUTHOR(S) David J. Larkin and Leonard V. Interrante					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM TO		14. DATE OF REPORT (Year, Month, Day) December 1991	
15. PAGE COUNT 10 pages					
16. SUPPLEMENTARY NOTATION To be published in: Amer. and Crystalline Silicon Carbide IV, M. Rahman, G. Harris, editors, Springer Proceedings in Physics					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Silicon carbide, Disilacyclobutanes, MOCVD, single-source precursor		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>Substituted 1,3-disilacyclobutanes were studied as potential low temperature single-source CVD precursors to silicon carbide. These studies were carried out in a cold-wall LPCVD system maintained at a total reactor pressure of 1.0 Torr using a mass flow controlled argon carrier gas. The precursor was decomposed on resistively heated Si(100) substrates at temperatures ranging from 700°C - 1100°C. Gas chromatography-Fourier transform infrared spectroscopy and quadrupole mass spectrometry were used to identify the volatile pyrolysis byproducts from each precursor. The decomposition onset temperature was separately determined for each precursor by monitoring the major pyrolysis byproducts, by using quadrupole mass spectrometry, while slowly increasing the substrate temperature. Scanning and transmission electron microscopy were used to determine the cross-sectional and surface morphology and also the deposition rate, which ranged from ca. 0.035 $\mu\text{m}/\text{h}$ to 12.0 $\mu\text{m}/\text{h}$.</p>					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. John Pazik			22b. TELEPHONE (Include Area Code) (703) 696-4410		22c. OFFICE SYMBOL

Studies of 1,3-Disilacyclobutanes as Single-source CVD Precursors to Silicon Carbide

David J. Larkin
NASA Lewis Research Center
Cleveland, OH 44126

Leonard V. Interrante
Rensselaer Polytechnic Institute
Troy, NY 12180


Abstract. Substituted 1,3-disilacyclobutanes were studied as potential low temperature single-source CVD precursors to silicon carbide. These studies were carried out in a cold-wall LPCVD system maintained at a total reactor pressure of 1.0 Torr using a mass flow controlled argon carrier gas. The precursor was decomposed on resistively heated Si(100) substrates at temperatures ranging from 700°C - 1100°C. Gas chromatography-Fourier transform infrared spectroscopy and quadrupole mass spectrometry were used to identify the volatile pyrolysis byproducts from each precursor. The decomposition onset temperature was separately determined for each precursor by monitoring the major pyrolysis byproducts, by using quadrupole mass spectrometry, while slowly increasing the substrate temperature. Scanning and transmission electron microscopy were used to determine the cross-sectional and surface morphology and also the deposition rate, which ranged from ca. 0.035 $\mu\text{m/h}$ to 12.0 $\mu\text{m/h}$.

1.0 Introduction

Research on the development of silicon carbide as a high temperature and high power semiconductor is continuing to gain momentum internationally.^{1,2} With the onset of commercially available 6H-SiC 1" wafers and the demonstration of blue LED operation at 350°C,³ it is evident that this technology will continue to develop as a viable source of semiconductor material for electronic device manufacture. A critical aspect of successful device manufacture is the ability to consistently produce high quality epitaxial layers. Stoichiometry control is typically accomplished with the use of separate mass flow controlled source gases, one for Si and another for C. Although there have been some reports of single-source precursors to SiC, a flow of hydrogen is usually required for efficient removal of excess carbon or chlorine, in the case of chlorocarbosilanes, and substrate temperatures typically exceed 1100°C.

Alternatively, we have undertaken a systematic study of various derivatives of 1,3-disilacyclobutane as a single-source CVD precursor to silicon carbide. These compounds have been shown to produce stoichiometric SiC in an inert atmosphere of argon at a relatively low deposition temperature (as low as 850°C).⁴ The correct SiC stoichiometry is

92 3 03 222

92-05759


"designed" into the four-membered $-(SiC)_2-$ ring structure, which contains a considerable amount of ring-strain and aids in obtaining a relatively low decomposition temperature. Upon decomposition, this ring opens with the possible formation of reactive species, where both the silicon and carbon can serve as reactive atomic centers. This assists in the incorporation of both the silicon and carbon into the growing film, thereby utilizing more effectively both the Si and C of the disilacyclobutane ring. We report here on selected aspects of this investigation of disilacyclobutane, and derivatives thereof, which includes a description of the molecular structures for each derivative, pyrolysis byproducts detected by GCFTIR and QMS, and film analysis by SEM, TEM, and FTIR.

2.0 Experimental

The disilacyclobutane derivatives I, II, and III were chemically synthesized either by directly using known literature preparations⁵⁻⁸ or modifications thereof. Each compound was purified by fractional distillation at atmospheric or reduced pressure, in a nitrogen environment. The purified compounds were characterized by using 1H , ^{29}Si , and ^{13}C Fourier transform NMR (FTNMR); FT infrared spectroscopy (FTIR); and quadrupole mass spectrometry (QMS). All three compounds are colorless liquids which are non-pyrophoric, but slowly oxidize when exposed to oxygen.

A schematic of the all stainless, turbo-pumped, cold-wall, hot-stage, low pressure CVD (LPCVD) apparatus that was used in the pyrolysis studies of these compounds is shown in Figure 1. Attached to the LPCVD apparatus is a QMS system which aided in the determination of the initial decomposition (onset) temperature for each compound, as described previously.⁹ For this determination, the mass peaks (m/e) which are characteristic of initial precursor decomposition (methane m/e = 15, 16; hydrogen m/e = 2, as determined in preliminary experiments) were monitored as the silicon substrates were slowly heated from room temperature.

The substrates (silicon wafer sections) were resistively heated via a DC current. The "as received" Si(100) substrates (Wacker Siltronic Co.; $\rho=1.1 \Omega \text{ cm}$; p-type; 525 μm thick) were scored on the unpolished face and then cleaved into 1.4 cm X 6.5 cm rectangular shaped pieces. Typically, two to three pieces were then connected in a series circuit by using tungsten clips and tantalum leads and subsequently loaded into the stainless steel reactor. A current-limited DC power supply was used as the power source to resistively heat the silicon and maintain the surface at temperatures ranging between 650°C-1150°C. The substrate surface temperature was determined by using the combination of an optical pyrometer and a previously calibrated thermocouple fastened to the silicon substrate.

Prior to each experiment, the entire LPCVD system was evacuated and backfilled using purified argon. A base pressure of ca. 5×10^{-8} Torr was reproducibly achieved with the apparatus walls maintained at 80°C and the silicon substrates at $> 800^\circ\text{C}$.

The volatile byproducts were condensed in a stainless steel, liquid- N_2



Dist	Special	for
A-1		

<input checked="" type="checkbox"/>
<input type="checkbox"/>
<input type="checkbox"/>

cooled trap, located downstream of the heated substrates, for later analysis by using Gas Chromatography-FTIR (Perkin-Elmer 1800 FTIR with an MCT detector; Varian 1500 GC using a VZ-10 column).

The resulting silicon carbide coated Si(100) pieces were analyzed for residual Si-H and C-H absorptions, indicative of partial decomposition of the precursor, by using FTIR in both the specular reflectance and transmission mode. An uncoated, unheated Si(100) piece was used for background subtraction.

Scanning electron microscopy was routinely used to examine the surface morphology of the deposited SiC films, whereas cleaved SiC/Si(100) samples were used to determine the film thicknesses and cross sectional morphologies. TEM was also employed to examine the SiC-film/Si(100) interface of a thin film (ca. 80 nm) which resulted from the decomposition of precursor (I) at the previously reported⁹ deposition onset temperature (755°C).

3.0 Results And Discussion

Chemical Structure of Precursors:

The molecular structure for 1,3-disilacyclobutane (III) and for the derivatives (I) and (II) are shown in Figure 2. In particular, note the four-membered $-(SiC)_2-$ "core-structure" common to all three of the precursors. This four-membered ring is of particular interest because of 1). the 1:1::Si:C stoichiometry "designed" into the ring structure 2). the significant amount of ring strain energy contained in the ring 3). the availability of both Si and C as very reactive centers, as a result of ring opening upon precursor decomposition.

The correct Si/C ratio for SiC is designed into the four-membered ring, which potentially eliminates the requirement for stoichiometry control through the use of mass flow controllers. By choosing both the proper substituents contained on the four-membered ring (i.e. methyl, hydrogen, chloro, etc.), which can be eliminated under the appropriate deposition conditions (e.g., methyl eliminated as methane), it is possible to produce stoichiometric SiC films.^{4,9} The relatively lower decomposition temperatures associated with the disilacyclobutanes is, in part, related to the strain contained in the four-membered ring. This ring strain arises because the four atoms contained in the ring are forced to adopt bond angles smaller, and therefore less stable, than the tetrahedral (109.5°) bond angle. For example, the ring strain energy has been calculated for the tetra-methyl substituted disilacyclobutane derivative as 24.6 ± 2.6 Kcal/mol.¹⁰

The remaining important feature of this class of compounds is the reactivity of both the Si and C atoms contained in the ring. Results of work by Auner, et al.¹¹ have indicated that the disilacyclobutane ring can thermally decompose to yield reactive intermediate fragments such as the π -bonded silene ($R_2Si=CH_2$)^{11,12} and the diradical species, silylene ($R_2\dot{Si}-\dot{C}H_2$). In both cases the Si and C atomic centers are reactive, which

aids in the incorporation of both the Si and C into the growing film. This helps to preserve the stoichiometry designed into the $-(\text{SiCH}_2)_2-$ four-membered ring structure.

Pyrolysis Byproducts:

Each compound was separately used as a LPCVD precursor in a set of similar experiments. After each set of experiments, involving one of the three precursors and carried out at different deposition temperatures, the byproducts that had condensed in the L-N_2 cooled trap (downstream of the reactor) were analyzed by GCFTIR. The non-condensable byproducts were analyzed during the course of the LPCVD experiment by using the QMS. The major pyrolysis byproducts from compounds (I) and (II) were methane and hydrogen, compared to compound (III) which produced only hydrogen as the major pyrolysis byproduct. The minor byproducts from compounds (I), (II), and (III) consisted of a mixture of various methylsilanes ($\text{H}_{4-x}\text{SiMe}_x$; $x = 1-4$). The amount of methyl substitution on the methylsilanes, for each precursor, was found to be directly related to, and limited by, the number of Si-C bonds contained in the molecular structure of each precursor. For example, compound (III) produced only methylsilanes of the form ($\text{H}_{2+x}\text{SiMe}_{2-x}$; $x = 0-1$), whereas compound (I) yielded ($\text{H}_x\text{SiMe}_{4-x}$; $x = 0-3$). This suggests that the pyrolysis byproducts are a result of discrete mechanistic decomposition pathways and are not produced from random recombination of radical species. Furthermore, methane is believed to be produced primarily from the methyl substituents and not from the $-(\text{CH}_2)-$ contained in the ring, which is supported by the lack of methane detected from the pyrolysis of compound (III).

The identities of the major pyrolysis byproducts were used to determine the decomposition onset temperature for each precursor. This was accomplished by monitoring the LPCVD reactor contents, as a function of an increasing substrate temperature, by using the attached QMS. The resulting plots of m/e peak intensities indicative of methane (for precursors I and II) and hydrogen (for precursor III) versus the Si(100) surface temperature were used to determine each precursor decomposition onset temperature. The series of decomposition onset temperatures (I{760°C}; II{740°C}; and III{680°C}) were determined to be inversely proportional to the amount of hydrogen substitution on the Si contained in the ring. This trend is consistent with a decomposition scheme described by Auner, et al.¹¹ which is based on the availability of the Si-H moiety within the four membered ring of disilacyclobutane derivatives. Auner, et al. describe a hydrogen shift decomposition mechanism which requires hydrogen to be present on the Si contained in the ring. In this scheme, hydrogen transfer from the "ring-Si" to an adjacent "ring-C" is energetically favorable, in part, due to the release of the ring strain energy.

Film Analysis:

The films produced from each of the three precursors were routinely analyzed by using SEM, FTIR, and powder XRD and selected films were examined at the Si/SiC interface by using TEM. SEM was used to examine the surface and cross-sectional morphology of the films deposited at different substrate

surface temperatures, which ranged from ca. 700°C to 1150°C. The surface and cross-sectional morphology appeared smooth and featureless at the lower deposition temperatures and became columnar in appearance at higher temperatures. The onset of the columnar growth occurred at a different temperature for each precursor, which in each case corresponded to the maximum deposition rate of ca. 12.0 $\mu\text{m}/\text{h}$. These observations are consistent with a transition from a kinetically controlled to a gas phase diffusion limited deposition.¹³

Fourier transform IR (FTIR) was used in both the specular reflectance and transmission mode to analyze for IR absorptions in the 1900 cm^{-1} - 2000 cm^{-1} and in the 2900 cm^{-1} - 3200 cm^{-1} regions. These spectroscopic regions correspond to Si-H_x and C-H_x, respectively, and absorptions in these regions would indicate incomplete decomposition of the precursor. Since no absorptions were detected in either of these regions then the concentration of A-H_x (A = Si or C) is less than the detection limit for FTIR or there is complete decomposition of the precursor on the substrate.

The film deposited from compound (I), at the decomposition onset temperature (760°C), was examined in cross-section at the Si/SiC interface by using high resolution TEM. The total thickness of the film is ca. 90 nm, consisting of a top amorphous layer (\approx 75.0 nm) and a polycrystalline β -SiC layer (determined by SAD) located at the Si/SiC interface. As shown in Figure 3, the silicon substrate contains a series of pits which are defined by the Si(111) planes. These pits are believed to have formed prior to the start of CVD, during an initial "bake-out" of the vacuum system which includes heating the substrate to ca. 800°C. Evidence for pit formation prior to the start of CVD is given in Figure 3(c.), which shows a continuous coating lining the inner surface of the pit. A TEM lattice image of the pit area revealed that this portion of the film was completely amorphous.

4.0 Conclusions

Derivatives of 1,3-disilacyclobutane were studied as potential single-source, low temperature (<1000°C) LPCVD precursors to polycrystalline silicon carbide films on Si(100) substrates. These compounds are non-pyrophoric and, under appropriate CVD conditions, pyrolyze to stoichiometric silicon carbide films in an argon environment. These compounds do not require the use of a co-reactant, such as hydrogen, as most other sources of CVD SiC commonly employ for complete removal of excess carbon, chlorine, or similar byproducts. Each precursor had a maximum deposition rate of 12 $\mu\text{m}/\text{h}$, which was consistent with a mass transport limitation. The correlation of the decomposition onset temperature for each compound with initial film formation suggests that reactive film-forming species are produced at these decomposition onset temperatures. This class of compounds show good potential as CVD precursors and will be studied further as potential CVD sources of SiC single crystal epitaxy at low (< 1000°C) temperatures.

Acknowledgments

The authors would like to thank J. Yang and Prof. P. Pirouz for their TEM expertise. This work was supported at RPI by the Chemistry Division of the Office of Naval Research.

References

- [1] Proceedings: First International High Temperature Electronics Conference, ed. by D. B. King, F. V. Thome (Albuquerque, N. Mex., June 1991).
- [2] Amorphous and Crystalline Silicon Carbide II, ed. by M. M. Rahman, C. Y.-W. Yang, Springer Proceedings in Physics, Vol. 43 (Springer-Verlag Berlin, Heidelberg, 1989).
- [3] Cree Research Inc., Durham, NC 27713.
- [4] D. J. Larkin, L. V. Interrante, Chem. Mater., in press.
- [5] W. A. Kriner, J. Org. Chem., 29, 1601(1961).
- [6] R. M. Irwin, J. M. Cooke, J. Laane, J. Amer. Chem. Soc., 99(10), 3273(1977).
- [7] N. Auner, J. Grobe, J. Organomet. Chem., 222, 33(1981).
- [8] N. S. Nametkin, V. M. Vdovin, V. I. Zav'yalov, P. L. Grinberg, Izv. Akad. Nauk. SSSR, Ser. Khim., 5, 929(1965).
- [9] D. J. Larkin, L. V. Interrante, J. B. Hudson, B. Han, Proc. M.R.S. Meeting; Chem. Perspec. Microelectr. Mater. II, ed. by L. H. Dubois, L. V. Interrante, M. E. Gross, K. F. Jensen (Mater. Res. Soc. Symp. Proc., 204, Pitts. PA 1991) p. 141.
- [10] H. E. O'Neal, M. A. Ring, J. Organomet. Chem., 213, 419(1981).
- [11] N. Auner, I. M. T. Davidson, S. Ijadi-Maghsoodi, F. T. Lawrence, Organomet., 5, 431(1986).
- [12] D. M. Brown, J. D. Parsons, US Patent No. 4 923 716 (8 May 1990).
- [13] J. M. Blocher Jr., in Vapor Deposition, ed. by C. F. Powell, J. H. Oxley, J. M. Blocher Jr. (John Wiley & Sons, Inc., New York 1966) p.11.

Figure 1: A schematic of the LPCVD system with an attached QMS; 1.) Carrier gas inlet, 2.) Mass flow controller, 3.) Stainless bubbler containing precursor, 4.) Capacitance manometer, 5.) Sapphire view port, 6.) Silicon substrates, 7.) Series of 3 cold traps, 8.) Sampling leak valve, 9.) Quadrupole mass spectrometer, 10.) Mechanical pump used to maintain the gas sampling flow, 11.) to the main L-N₂ cooled trap and pumping system.

Figure 2: The chemical structure of the three disilacyclobutane compounds used as precursors for the production of silicon carbide thin films: a.) 1,3-Dimethyl-3-methylsilamethylene-1,3-disilacyclobutane; b.) 1,3-Dimethyl-1,3-disilacyclobutane; c.) 1,3-disilacyclobutane.

Figure 3: Cross-sectional TEM of the film produced from the decomposition of compound (I) at the decomposition onset temperature of 760°C. This micrograph reveals the a.) amorphous region, b.) polycrystalline SiC layer at the SiC/Si(100) interface, and c.) the continuous amorphous layer lining the pit that formed in the silicon substrate.

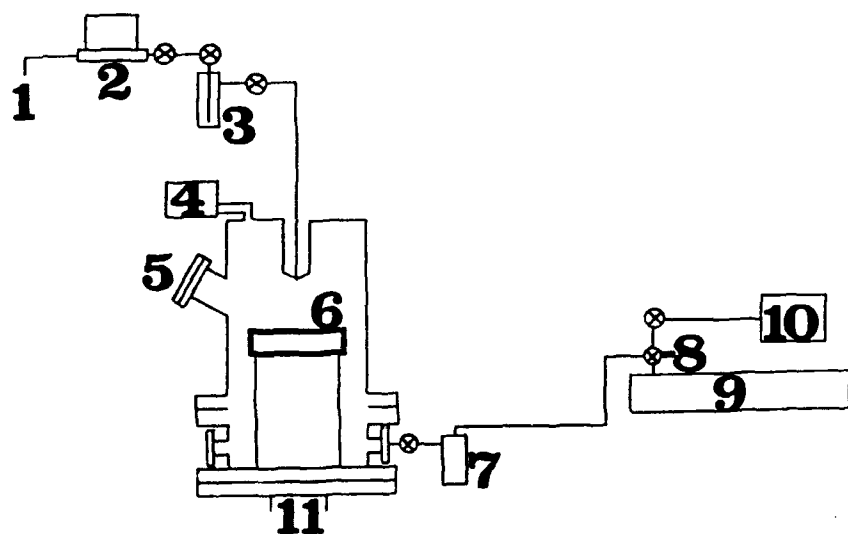


FIG 1 . D. J. Larkin, L. V. Intervante

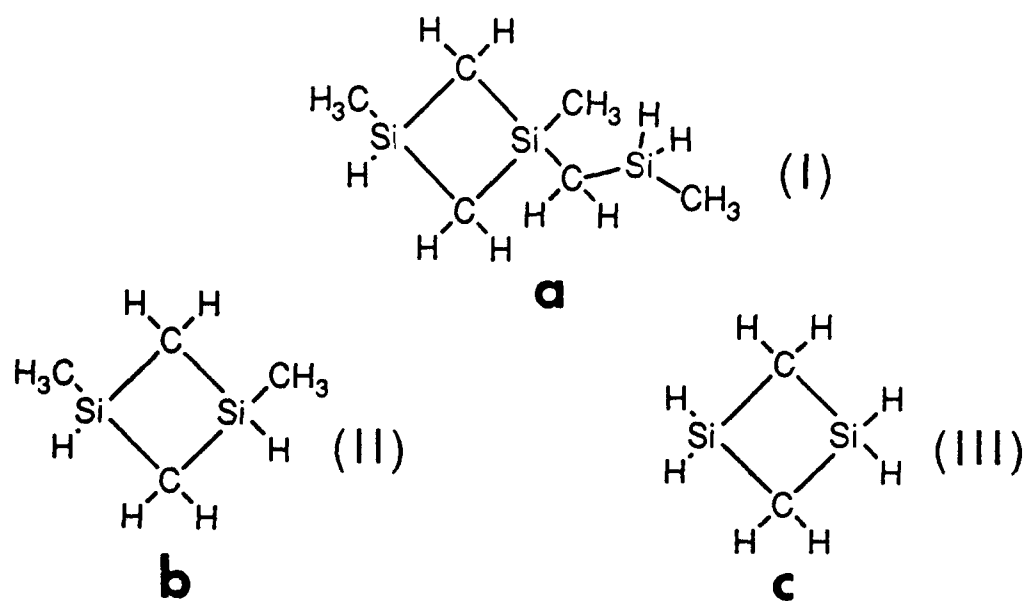


FIG 2 D. J. Larkin, L. V. Interrante

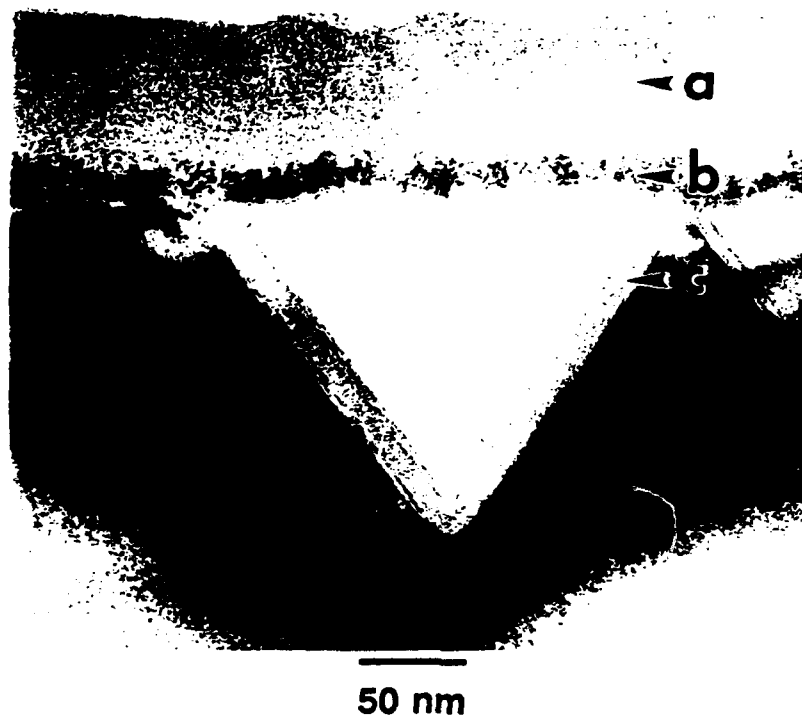


FIG 3: D.J. Larkin , L.V. Interrante